A Novel Concept of Symmetry in Model of Fluctuational Thermodynamics

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The conventional statements of scaling theory are: 1) that the coexistence curve (CXC) of real fluids does not possess any immediately apparent symmetry as well as the CXC of van der Waals (vdW -) model; 2) the lattice - gas (LG -) model belongs to the same class of universality as the real fluids and it has the line of symmetry which is identical with the critical isochore ρ_C; 3) it is necessary to make use of transformation from measured reduced variables (temperature: $\overline{T} = T/T_C - 1$, density: $\overline{\rho} = \rho/\rho_C - 1$) to some parametric variables (the remoteness from a critical point: r and the order parameter: θ) of linear model proposed by Schofield to describe the asymptotic LG -symmetry of real fluids near the critical point. Despite widespread belief to the contrary, we intend to demonstrate that all of the above - named systems (LG - model, real fluids, vdW - model) have a common line of symmetry - critical isochore coincided with the reduced rectilinear diameter: $(\rho' + \rho'')/2\rho_C$, within the wide range: $\pm 0.25\rho_C$ of two - phase region. The necessary condition of doing it is the transformation from reduced temperature $\overline{T}$ to the reduced difference of specific entropies: $\overline{s} = M(s'' - s')/2R$ used as a parameter of disorder in the fluctuational thermodynamics (FT -) model, proposed by one of the authors. Each specific one - phase isentrop s has in the FT - model a special significance of one of the characteristic curves of a thermodynamic surface. There is a particular thermodynamic (T -) symmetry of changing along this curve of the pairs of conjugated variables (fields: μ, T and densities: ρ, σ) for a local potential - pressure P. The FT - model describes reasonably well the thermophysical properties in a whole fluid region and can be used for analysis of T - symmetry globally(i. e. taking into account the presence of two - phase region). It is a known fact that Gibbs solved the vdW - model together with Maxwell's equal area rule in a parametric form. One can verify that the parameter in this solution is the same dimensionless variable $\overline{s}$ which is used in the FT - model. The densities of both phases expressed in terms of the parameter $\overline{s}$ along the CXC of the vdW - model have an ideal symmetry (zero slope of rectilinear diameter) and, simultaneously, a discontinuity in the critical point. The similar ideal symmetry and discontinuity there are for the real substances as we have found for Ar, C_2H_4, CO_2 and H_2O measured data. The LG - model has in this co-ordinates ($\overline{\rho}$, $\overline{s}$) only asymptotic symmetry because the parameter $\overline{s}$ is identically equal to zero in this model. As the similar line of symmetry has been identified in all above-named different systems we must conclude some paradoxically that the real fluids are much more similar in this sense to the vdW - model than to the LG - model. It is possible that the adequate description of the fluid properties can be achieved only by a superposition of the vdW - model (short - ranged repulsion) and LG - model (short - ranged attraction) up to the critical point itself. The FT - model is a possible variant of a such an approach.